

Anion Exchange in Mixed Solvent Systems. I. Study of the Equilibrium Distribution

V. KOPRDA, M. FOJTÍK, and M. SZLAUROVÁ

*Research Institute of Industrial Hygiene and Occupational Diseases,
Bratislava 1*

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The distribution of chloro complexes of corrosion and fission products between anion exchanger and mixed solvent systems was studied by static ion exchange method. Attention was paid to the dependence of this process on the proportion and character of individual components in mixed solutions.

The values of equilibrium distribution coefficients were determined for the chloro complexes of 18 most important radionuclides of corrosion and fission products in systems: anion exchanger Dowex 2X-8—water—hydrochloric acid—methanol, ethanol or acetone. These measurements were carried out in the whole concentration range of individual components.

The use of ion exchangers for the separation of individual ions from complicated mixtures or their fractionation in groups is of growing importance. Because of a greater variability of equilibrium distribution coefficients, the mixed organic-aqueous solvent systems used for the separation of complex ionic forms of substances are preferred to the aqueous solutions of complex-forming substances.

The study of the exchange of complex ions by anion exchangers has shown that the presence of organic solvent in the system often results in increased sorption and better separation. In the case of the sorption from a mixture of organic solvents and inorganic acid most attention was paid to hydrochloric acid. An addition of considerable amounts of organic solvents miscible with water to aqueous solutions of hydrochloric acid usually results in a greater sorption of metals by anion exchanger or in an equal sorption at lower concentrations of hydrochloric acid. In most cases the sorption of the elements subjected to considerable sorption even in aqueous solutions of hydrochloric acid were investigated.

Aliphatic alcohols [1–16] and ketones (acetone) [4, 5, 17–21] in combination with hydrochloric acid are the organic solvents most frequently used for the separation of various metallic ions on anion exchangers. The use of other organic solvents is relatively scarce [22, 23].

Korkisch and *Janauer* [6], *Poitrenaud* [24], *Prášilová* [25], and more recently *Korkisch* [26] and *Moody et al.* [27] gave a general analysis of the problems involving the effect of organic solvent on the sorption on ion exchangers as well as a review of the papers dealing with the problems of ion exchange from mixed solvent systems.

Provided a part of water in solvent system is replaced by organic solvent, the properties of solution and exchanger are influenced. The sorption of solvent and swelling of exchanger, distribution of complex-forming agent, solvation of mobile and fixed ions, activity and association of electrolytes, equilibria in the series of arising complex com-

pounds and affinity with respect to ionic and molecular exchange are altered. The degree to which the equilibrium states and the velocity of their establishment is influenced depends on the character of exchanged ion, the anion exchanger, and the solvent mixture used. A general analysis of the effect of organic solvent on the exchange system and the ion exchange equilibria has been given in previous paper [28].

An exact description of the ion exchange behaviour of complex anions in mixed organic-aqueous solutions is complicated by the lack of basic physicochemical data on the ions in solution and exchanger.

The complex judgement of the papers referred to has shown that in spite of the insufficient theoretical fundamentals the ion exchange of complex anions from mixed organic-aqueous solutions is more and more used for solving various difficult analytical problems. It appears that it is also an analytical method suited for various complicated mixtures of fission and corrosion products.

Experimental

Material, instruments, and equipments

For the preparation of mixed solvent systems methyl alcohol, ethyl alcohol (96 weight %), acetone, concentrated hydrochloric acid, and distilled water were used.

The commercial grade radionuclides supplied by ÚVVVR were applied. The stock solutions of radionuclides contained the activity of 10–20 $\mu\text{Ci ml}^{-1}$ and the following amounts of isotopic carriers: ^{46}Sc 5.9 $\mu\text{g ml}^{-1}$, ^{51}Cr 23 $\mu\text{g ml}^{-1}$, ^{54}Mn without carrier, ^{59}Fe 1.3 $\mu\text{g ml}^{-1}$, ^{60}Co 5 $\mu\text{g ml}^{-1}$, ^{64}Cu 0.5 $\mu\text{g ml}^{-1}$, ^{65}Zn 7.6 $\mu\text{g ml}^{-1}$, ^{86}Sr without carrier, ^{91}Y without carrier, ^{95}Zr without carrier, ^{95}Nb without carrier, ^{99}Mo 4.4 $\mu\text{g ml}^{-1}$, ^{106}Ru without carrier, ^{137}Cs without carrier, ^{140}La 0.02 $\mu\text{g ml}^{-1}$, ^{140}Ba without carrier, ^{144}Ce 0.7 $\mu\text{g ml}^{-1}$, ^{152}Eu 6.9 $\mu\text{g ml}^{-1}$, ^{181}Hf 1.7 $\mu\text{g ml}^{-1}$.

Anion exchanger Dowex 2X-8 (100–200 mesh) in Cl^- form was employed. The particles below the lower limit of graininess of the exchanger were removed by countercurrent sedimentation. The suspension of exchanger was heated to 60°C and degassed by a water pump. The anion exchanger was several times cyclically transformed into the forms $\text{Cl}^- - \text{OH}^- - \text{Cl}^-$, washed with distilled water, dried at 60°C, and kept in desiccator over silica gel. After shaking, the phases were separated in a vessel with a porous glass bottom.

The activity measurements of liquid samples were carried out in 5-ml thin-walled glass ampoules Str-5 by means of a well-type scintillation crystal. The activity measurements of the exchanger were performed after separation of liquid phase right in the vessel with porous glass bottom which was placed on the scintillation crystal. The activity measurements of β -emitters (^{86}Sr and ^{91}Y) were made on the discs of filtration paper confined by 30-mm paraffin border by a Geiger–Müller counter.

In all cases the relative activities were measured. The measurements were so made that the relative error was smaller than 1% and the time of measurement might not exceed 5 minutes.

Methods

For the determination of equilibrium distribution coefficients the batch method was used. The exchange system consisted of the anion exchanger Dowex 2X-8 (100–200 mesh) and the mixed solution. The mixed solutions were prepared volumetrically by mixing respective amounts of methyl alcohol, ethyl alcohol, or acetone with corresponding

amounts of concentrated hydrochloric acid and distilled water. The volume contraction of mixtures was not considered. The mixed solutions contained 40, 55, 65, 75, 85, and 95 volume % of organic solvent. The concentration of complex-forming agent was fixed by dosing the concentrated hydrochloric acid so that the final molarity in the series of mixed solutions increased by 0.25, 0.50 or one unit. Into each mixed solution 1 ml of the stock solution of a certain radionuclide was added. After thorough mixing, each solution was divided into two portions (15 and 35 ml) in 50-ml volumetric flasks. The dry anion exchanger was added both to the first and to the second portion (0.5 and 1.0 g, respectively).

The exchange systems thus prepared were shaken twice for 2 hours with an interruption of 16 hours. After the establishment of equilibrium state the activity of aliquot parts of the solution was measured. The activity of mixed solutions before the addition of exchanger into the mixed solution was determined by graphical interpolation using the solutions containing the components of mixed solution and the same concentration of radionuclide as the investigated solutions before the exchange process.

The equilibrium distribution coefficient was determined from the activity decrease of the external solution before and after the establishment of equilibrium state

$$K_d = \frac{A_0 - A_e}{A_e} \frac{V}{w_1}, \quad (1)$$

where A_0 — activity of 1 ml of external solution before the addition of ion exchanger [des. min⁻¹ ml⁻¹],

A_e — activity of 1 ml of external solution after the establishment of ion exchange equilibrium [des. min⁻¹ ml⁻¹],

V — volume of external solution [ml],

— mass of dry exchanger in the exchange system [g].

When the distribution of ⁹⁵Zr and ¹⁸¹Hf was studied, the activity of exchanger was also measured right in the vessel with porous glass bottom by sucking off the external solution. Some corrections were made with respect to the geometry change during the measurements. The equilibrium distribution coefficient was then determined by means of the formula

$$K_d = \frac{A_r}{A_e}, \quad (2)$$

where A_r is the activity of exchanger phase after the establishment of equilibrium state [des. min⁻¹ g⁻¹].

All experiments were carried out at laboratory temperature.

Results and Discussion

Using the above procedure the values of equilibrium distribution coefficients on the anion exchanger were determined for Cr, Mn, Co, Fe, Cu, Zn, Ba, Sr, Sc, Y, La, Ce, Eu, Hf, Nb, Zr, Mo, and Ru in the medium water—hydrochloric acid—methyl alcohol or ethyl alcohol or acetone. The results are given in Figs. 1–3 which show the dependence of logarithm of the equilibrium distribution coefficient on the concentration of complex-forming agent for varying content of the organic solvent in mixed solution.

The experiments with investigated radionuclides were carried out without any addition of carrier. The amount of carrier present in the exchanger at equilibrium was smaller

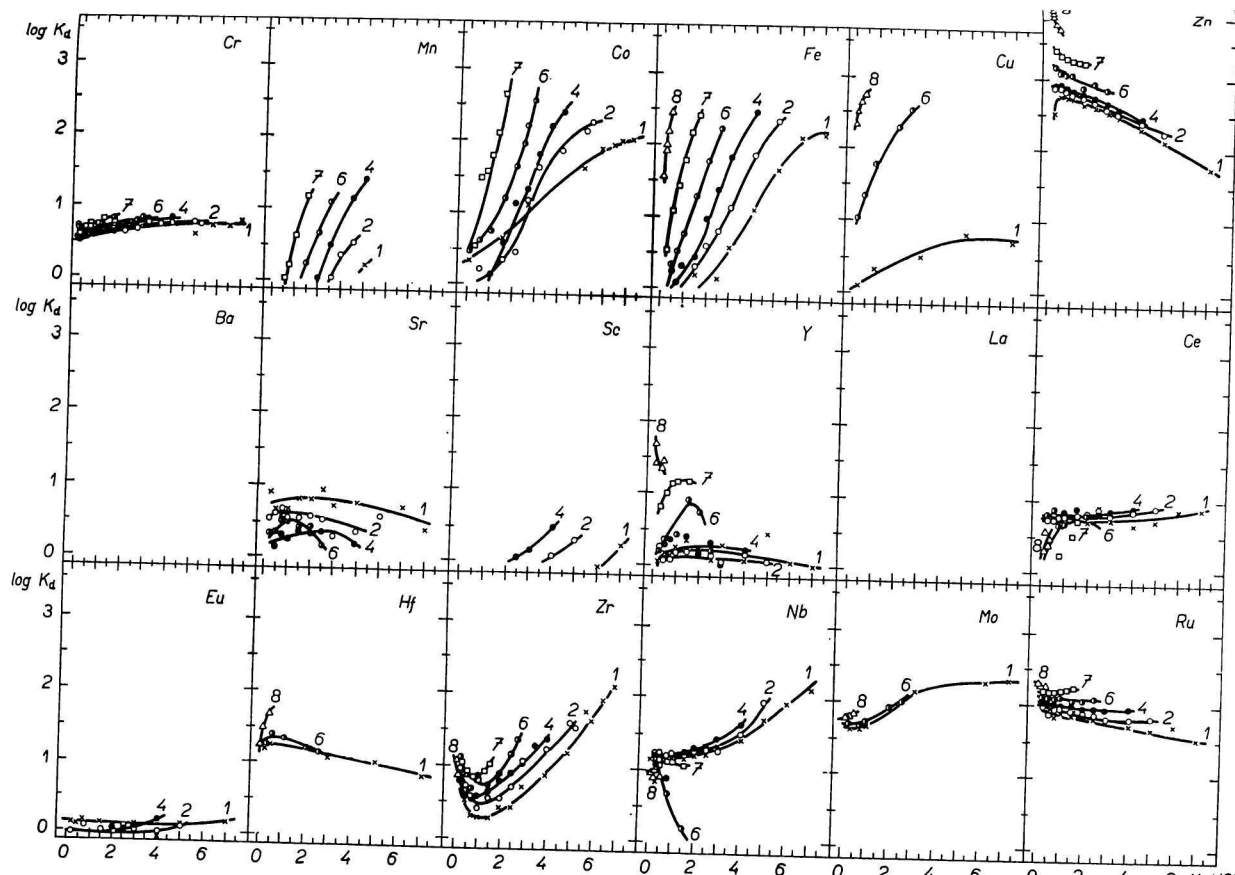


Fig. 1. Variation of the logarithm of equilibrium distribution coefficient of the radionuclides of corrosion and fission products with the concentration of hydrochloric acid in the system: anion exchanger Dowex 2X-8 (100–200 mesh) and mixed solvent system containing methyl alcohol. 1. 40%; 2. 55%; 4. 65%; 6. 75%; 7. 85%; 8. 95%.

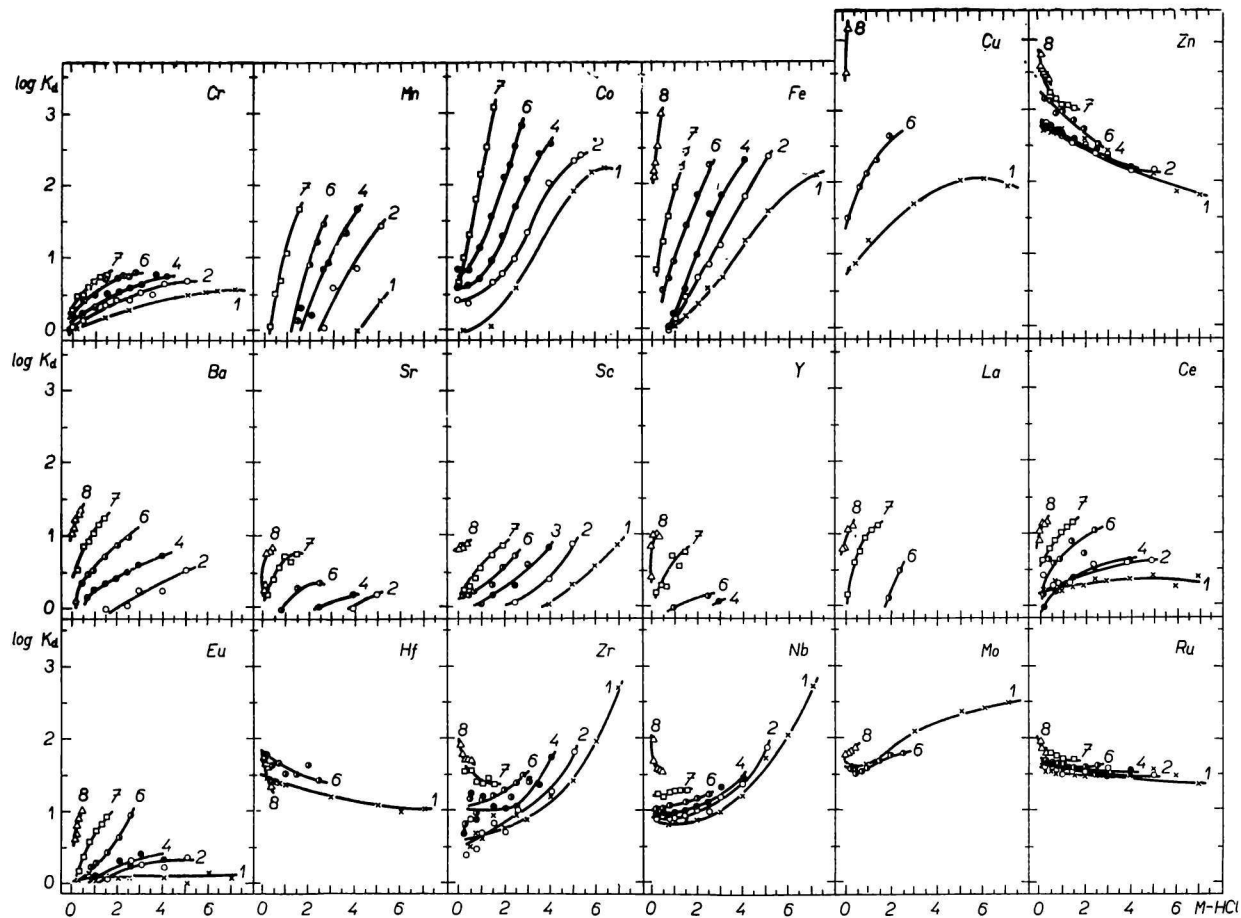


Fig. Variation of the logarithm of equilibrium distribution coefficient of the radionuclides of corrosion and fission products with the concentration of hydrochloric acid in the system: anion exchanger Dowex 2X-8 (100—200 mesh) and mixed solvent system containing ethyl alcohol.

1. 40%; 2. 55%; 3. 60%; 4. 65%; 5. 75%; 6. 75%; 7. 85%; 8. 95%.

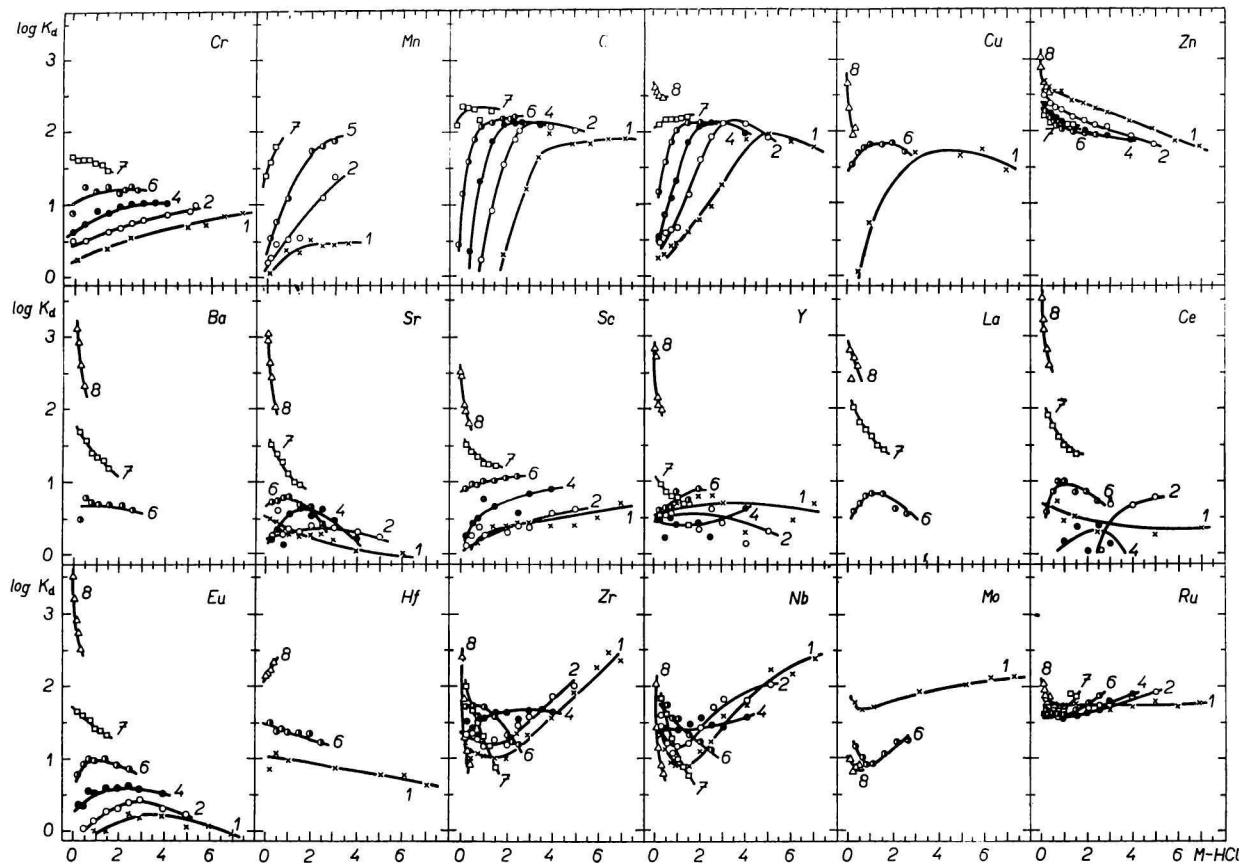


Fig. 3. Variation of the logarithm of equilibrium distribution coefficient of the radionuclides of corrosion and fission products with the concentration of hydrochloric acid in the system: anion exchanger Dowex 2X-8 (100—200 mesh) and mixed solvent system containing acetone.

1. 40%; 2. 55%; 4. 65%; 5. 70%; 6. 75%; 7. 85%; 8. 95%.

than 0.5% of total capacity of the exchanger. The limiting values of K_d which could be determined with the experimental equipment used are 5×10^{-1} and 3×10^3 . The deviations of the K_d values in parallel experiments were 5–20%. The experimental points in figures always express the average values of K_d calculated from two parallel experiments.

It is obvious that the values of equilibrium distribution coefficients are largely influenced not only by the kind but also by the amount of organic solvent in the mixed solvent system. The value of equilibrium distribution coefficient K_d usually increases with the increasing content of organic solvent. Furthermore, it increases with decreasing dielectric constant of mixed solution in the sequence methyl alcohol—ethyl alcohol—acetone.

Moreover, Figs. 1–3 show that the increasing content of hydrochloric acid in the mixed solvent system effects the transformation of particular forms of radionuclide in general in the following order: hydrolyzed forms (Zr, Nb) in ionic forms, positively charged ionic complexes in neutral ones, and neutral ionic complexes in negatively charged ones.

A comparison of the results presented in Figs. 1–3 indicates that the sorption of alkaline and alkaline earth elements in the solutions containing a high percentage of acetone is considerably higher than that in mixed solutions containing methyl alcohol or ethyl alcohol.

The character of the dependence of equilibrium distribution coefficient on the concentration of hydrochloric acid in mixed solvent system changes with increasing content of acetone. At higher values of dielectric constant of mixed solution the values of equilibrium distribution coefficient increase with the concentration of hydrochloric acid and conversely they decrease at lower values of dielectric constant.

For a greater part of the relationships stated a sorption of neutral complexes may be assumed. To simplify the thermodynamic treatment and to leave positively charged substances out of consideration it may be assumed that the distribution of the metal ion bound in complex with monodentate ligands X^- between the exchanger phase and mixed solution is governed by the following expression [29]

$$\log K_d = -\frac{\Delta F^0}{RT} + \log \frac{\beta_n(X^-)^n}{1 + \beta_1(X^-) + \beta_2(X^-)^2 + \dots + \beta_n(X^-)^n} + K, \quad (3)$$

where β_1 – β_n are the overall constants of the successive formation of complexes, K is a constant supposing that the concentration of ligand in the phase of exchanger does not change significantly owing to sorption. ΔF^0 denotes the change in free energy for the transition of neutral complex from the solution phase into the exchanger phase, which is proportional to the solvation of complex and increases with the molar fraction of organic solvent in mixed solution. The value of the logarithmic expression in relationship (3) thus changes almost linearly with the molar fraction of organic solvent in mixed solvent system.

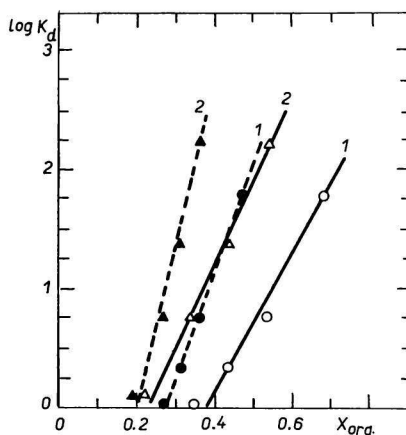
This assumption was confirmed by the investigation of equilibrium distribution of a microcomponent in the case of anion exchanger and mixed solvent systems. Figs. 4–6 show that the dependence of the logarithm of distribution coefficient on the molar fraction of solvent in both the inner and the outer solution of exchanger [30] is linear at constant concentration of hydrochloric acid. This fact indicates that a large part of microcomponent might be in the form of neutral complex in most systems under investigation.

The equilibrium distribution of microcomponent between the exchanger and neighbour-

Fig. 4. The logarithm of the equilibrium distribution coefficient of Fe as a function of the molar fraction of methyl alcohol in mixed solution.

1. 1 M-HCl; 2. 2.5 M-HCl.

○ outer solution; ● inner solution of exchanger.



ing solution is, in principle, governed by the relative proportions of individual kinds of the ions containing the microcomponent as well as by the properties of these ions in the pertinent medium, including exchange affinity.

The equilibrium distribution of the microcomponent, which occurs in various complex forms in the systems containing organic solvent, complex-forming agent, and anion exchanger, is determined by a set of coherent relationships. Moreover, the ion exchange is complicated by the fact that a part of water in solvent system is replaced by organic solvent.

When a part of water is replaced in mixed solvent system, a partial dehydration of ions takes place what enhances interionic exchange and association. The presence of

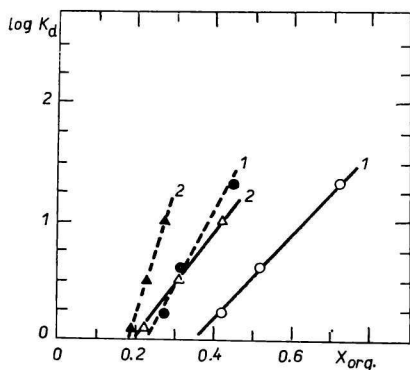


Fig. 5. The logarithm of the equilibrium distribution coefficient of Cr as a function of the molar fraction of ethyl alcohol in mixed solution.

1. 0.25 M-HCl; 2. 1 M-HCl.

○ outer solution; ● inner solution of exchanger.

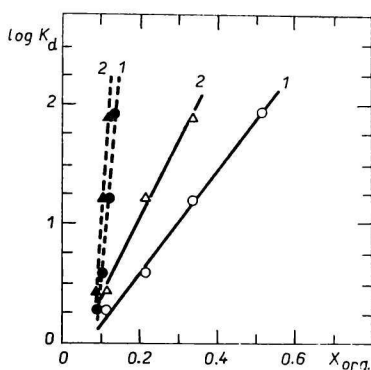


Fig. 6. The logarithm of the equilibrium distribution coefficient of Mn as a function of the molar fraction of acetone in mixed solution.

1. 1 M-HCl; 2. 2.5 M-HCl.

○ outer solution; ● inner solution of exchanger.

organic solvent reduces the dielectric constant in the phase of solution and favours the association of ions and electrolytes in the inner solution of exchanger. It may be supposed that the stability of complex ions increases in such medium.

The problem of equilibrium distribution of complex ions of the microcomponent is further complicated by the changes in the relative proportions of individual complex forms. At a given temperature the relative proportions are determined by the composition of solvent system. In view of the different physicochemical characteristics of the outer and inner solution of exchanger it may be expected that a change in the relative proportions of individual complex forms appears after their sorption on exchanger.

The equilibrium distribution of individual complex forms of ions of the microcomponent on the anion exchanger is governed by the constants of selectivity which express the exchange affinity of individual pairs of ions interchanging their positions.

An exact expression of the equilibrium in the system mixed solvent – anion exchanger is the Gibbs – Donnan relationship

$$\ln a_j - \ln(\bar{a}_j)\bar{n}_j = \frac{P\bar{v}_j}{RT}, \quad (4)$$

where a_j – activity of the species j in outer solution,

\bar{a}_j – activity of the species j in exchanger,

\bar{n}_j – number of moles of the species j in exchanger.

P – swelling pressure,

\bar{v}_j – partial molar volume of the species j in exchanger.

R – gas constant,

T – absolute temperature.

Since the theory of electrolytes gives only approximate expressions for the calculation of activity in mixed solutions of electrolytes and, in addition, only for the simplest mixtures of alkaline halogenides or hydrogen halogenides in water solutions, it appears that the Gibbs – Donnan equation of the ion exchange yields a very complicated expression when applied to a system containing mixed solvent, complex-forming substance, and negative, neutral, and positive forms of the microcomponent.

Many approximate relationships may be deduced for a quantitative description of the sorption of complex ions by anion exchanger. *Trémillon* [31] takes into account the exchange of complex anions and neutral complex. The total quantity of individual complex forms in a certain phase is expressed by means of the concentration of neutral complex, the dissociation constants of individual complex forms and the concentration of ligand. By expressing the equilibrium concentrations of complex ions in exchanger by the formal equilibrium constants the following relationship is obtained:

$$K_r = \frac{K_{MA_z/A^-}^c + K_{MA_{z+1}/A^-}^c \bar{C}_V + \dots + K_{MA_{z+n}/A^-}^c \bar{C}_V^n}{\frac{k_1^c k_2^c \dots k_z^c}{C_{A^-}^z} + \frac{k_z^c}{C_{A^-}} + 1 + \frac{C_{A^-}}{k_{z+1}^c} + \dots + \frac{C_{A^-}^n}{k_{z+1}^c k_z^c k_{z+n}^c}} \quad (5)$$

The individual symbols stand for:

K_r – distribution coefficient,

K^c – formal equilibrium constant of the interchange of corresponding complex form for a counter-ion of exchanger,

$k_1^c, k_2^c, \dots, k_{z+n}^c$ – relative constants of the successive dissociation of complex forms $MA_1^{(z-1)+}, MA_2^{(z-2)+}, \dots, MA_{z+n}^{n-}$,

- C_{A^-} — concentration of ligand in outer solution,
 \bar{C}_F — concentration of interchangeable counter-ions in exchanger.

It follows from expression (5) that the maximum value of distribution coefficient is obtained in the concentration range $k_2^c < C_{A^-} < k_{z+1}^c$, where the maximum amount of neutral complex is formed [32].

The sorption of elements on anion exchangers may be carried out by the following mechanisms:

a) In the neighbouring solution some anion complexes appear and may be exchanged for counter-ion of exchanger.

b) Neutral complexes which diffuse into exchanger and form with a counter-ion of exchanger a complex with a greater number of ligands arise in preference in the neighbouring solution.

c) In the neighbouring solution some cation complexes are formed. These complexes go over the interface and are transformed into neutral forms under the conditions existing in the bulk of exchanger. The neutral forms are not subjected to the limitations which ensue from the existing gradient of the counter-ions of exchanger.

Figs. 1—3 give the plots which express the dependence of the equilibrium distribution coefficient of certain radionuclides on the concentration of hydrochloric acid for different contents of organic solvent in mixed systems. On the basis of these plots it may be assumed that a few basic types of distribution process are in operation.

A. The equilibrium distribution coefficient increases with increasing concentration of complex-forming agent. In this case the beginning formation of chloro complexes and increased portion of the metal in a form prone to sorption may be assumed. In this concentration range of complex-forming agent the formation of some positively charged complexes which change to neutral or negative ones either in inner solution of exchanger or through direct interaction with interchangeable counter-ion may be supposed.

B. In the region where the plot of equilibrium distribution coefficient against the concentration of complex-forming agent has a maximum, we may presume that the neutral forms of chloro complexes are prevalingly responsible for the sorption.

C. Provided the value of equilibrium distribution coefficient continues to decrease with increasing concentration of hydrochloric acid beyond the maximum, the sorption of negative complexes is effective.

D. If the plot shows a minimum (*e.g.* the case of Zr or Nb), the process of ion exchange is likely complicated by the processes of physical sorption, hydrolysis, and partial precipitation of the element on ion exchanger.

The results obtained by the determination of the average ligand numbers of Ba and Ce [30] show that chloro complex is not formed in the phase of outer solution at low concentration of hydrochloric acid in mixed solution provided the content of organic solvent is high. On the other hand, some neutral complex forms appear in the phase of the inner solution of exchanger. These facts explain the surprisingly high sorption of alkaline and rare earth elements on anion exchanger.

Furthermore, the increasing content of organic solvent involves a decrease in the dielectric constant of medium and a rise in the value of the average ligand number of cobalt what indicates a shift in the series of the ion kinds formed in favour of the formation of complexes.

The equilibrium distribution coefficients increase under equal conditions (the concentration of hydrochloric acid and the content of organic solvent in mixed solvent system) in the order methyl alcohol—ethyl alcohol—acetone. This phenomenon may be due to the values of dielectric constant of mixed solutions which decrease in the same suc-

cession. The decrease in the dielectric constant of medium effects partial dehydration of ions which promotes the stepwise formation of complexes with increasing numbers of acid ligand groups and raises the affinity of exchanged substances with respect to exchanger.

The values of the ligand numbers of alkaline and alkaline earth metals favour the sorption of positively charged complex forms by anion exchanger. In view of the value of dielectric constant in the phase of inner solution of exchanger there are formed some complexes with a counter-ion of a functional group of exchanger. This mechanism may explain the values of equilibrium distribution coefficient in mixed solutions containing acetone (Fig. 3) where the very high values of equilibrium distribution coefficients of alkaline and alkaline earth metals are observed while their sorption is negligible in aqueous and alcoholic media.

In general, it may be stated that the dependence of equilibrium distribution coefficient on the composition of mixed solution (Figs. 1–3) has a characteristic course both for the groups of similar radionuclides (rare earth metals, alkaline earth metals, transition metals) and different organic solvents in mixed solution.

The results of the study of the sorption of radionuclides of corrosion and fission products provide comprehensive data for a design of separation procedures on the basis of anion exchangers from mixed solvent systems.

A more thorough appreciation of the mechanism of the ion exchange of chloro complexes from mixed solvent systems is feasible after a detailed study of the exchanger properties as well as of the forms of microcomponent in outer and inner solution of exchanger.

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